

Thermodynamic Study of the $\alpha \rightarrow \beta$ Phase Transformation in Titanium by a Pulse Heating Method*

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Measurements of the temperature and energy of the $\alpha \rightarrow \beta$ transformation, and the electrical resistivity near and at the transformation point of titanium by means of a subsecond duration pulse heating technique are described. The results yield 1166 K for the transformation temperature and $4170 \text{ J} \cdot \text{mol}^{-1}$ for the transformation energy. Electrical resistivity is found to decrease by about 9 percent during the $\alpha \rightarrow \beta$ transformation. Estimated inaccuracies of the measured properties are: 7 K for the transformation temperature, 5 percent for the transformation energy, and 2 percent for the electrical resistivity.

Key words: Electrical resistivity; high-speed measurements; high temperature; solid-solid phase transformation; thermodynamics; titanium; transformation energy; transformation temperature.

1. Introduction

A rapid pulse heating technique has been successfully used in earlier studies of solid-solid phase transformations in iron [1],¹ zirconium [2] and hafnium-3(wt. %) zirconium [3]. Because of the relatively short measurement times (less than one second), the method tends to minimize the difficulties associated with quasi steady-state experiments arising from heat loss, evaporation and, in particular, from chemical reactions which become a major problem when dealing with the Group IVB elements. In this paper, the same technique is applied to the measurement of temperature and energy of the $\alpha \rightarrow \beta$ phase transformation (from hexagonal close-packed to body-centered cubic) in titanium as well as its electrical resistivity in the neighborhood of the transformation point.

The method involves measuring the specimen temperature, the current through and voltage across the specimen as it undergoes rapid resistive self-heating from room temperature to high temperatures (about 1300 K) in less than 1 s. The temperature is measured by means of a high-speed photoelectric pyrometer [4]. The current through the specimen is determined by measuring the voltage across a standard resistance in series with the specimen. The voltage across the middle one third of the specimen is measured between spring-loaded knife edge probes. These quantities are recorded digitally every 0.4 ms with a full scale resolution of about 1 part in 8000. Details regarding the construction and operation of the measurement system and other pertinent information such as error analysis, etc. are given in earlier publications [5, 6].

2. Measurements

Typical analysis of the specimen material by the manufacturer indicate that it was 99.9+ percent pure, containing the following impurities (in ppm by weight): O, 360; Zr, 30; Fe,

Ni, Cu, 20 each; C, 15; Al, S, 10 each; Si, V, Mn, Sn, 5 each; Cr, 3; H, 3; N, 2; all other detected elements were less than 1 ppm each. The material was supplied in the form of cylindrical rods from which three tube-shaped specimens were fabricated by an electroerosion technique. The nominal dimensions of the tubes were: length, 75 mm; outside diameter, 6.4 mm; wall thickness, 0.5 mm. A rectangular sighting hole ($0.5 \times 1 \text{ mm}$) was machined through the wall at the middle of each tube thereby enabling pyrometric temperature measurements to be made under approximate blackbody conditions. The outer surfaces of the specimens were polished to reduce heat loss due to thermal radiation.

The high-speed pyrometer, which had been designed primarily for measurements above 1500 K, yielded somewhat noisy signals when used in the range 1100 to 1300 K. The calibration of the pyrometer, against a tungsten filament standard lamp (which had been calibrated, in turn, against the NBS "Temperature Standard") indicated that the standard deviation of an individual temperature measurement in the neighborhood of 1165 K is about 3 to 4 K.

As discussed elsewhere [7, 8], multiple cycles of heating and cooling through the transformation point were found to produce undesirable distortions in the tube-shaped titanium specimens. The values reported in this paper correspond to the first experiment for each specimen, for which no correction was needed. All the experiments were performed with the specimens in an argon environment at atmospheric pressure. The duration of the current pulses was typically about 480 ms and the heating rates were approximately $2600 \text{ K} \cdot \text{s}^{-1}$.

An oscilloscope trace photograph showing the time variation of the specimen radiance, as seen by the pyrometer during a typical heating experiment, is presented in figure 1. The plateau in the heating curve indicates the $\alpha \rightarrow \beta$ transformation.

Figure 2 shows the true temperatures of a specimen plotted as a function of time near and during the transformation. The dashed lines represent least-squares fits to the rapidly increasing temperatures before and after the transformation, as well as the mean temperature during the transformation

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¹ Figures in brackets indicate the literature references at the end of this paper

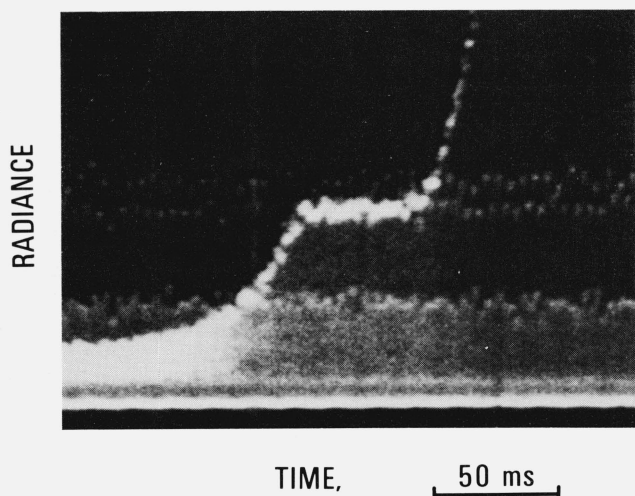


FIGURE 1. Oscilloscope trace photograph of specimen radiance (as measured by the pyrometer) near and at the $\alpha \rightarrow \beta$ transformation point of titanium (Specimen 3). Dots forming the long horizontal lines correspond to radiances from a reference source.

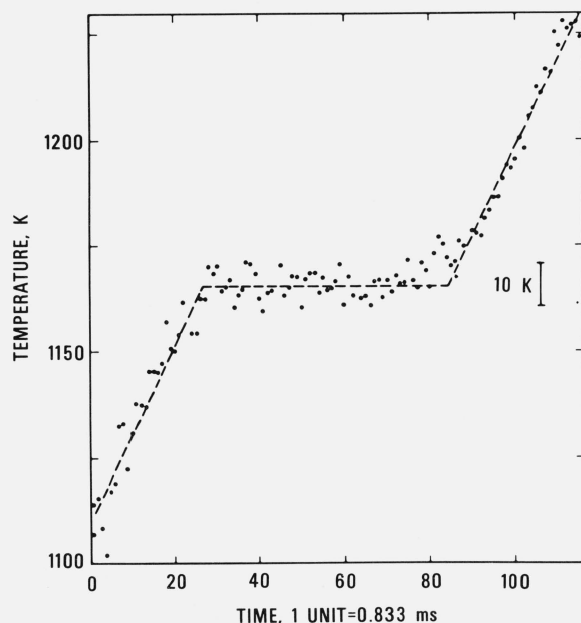


FIGURE 2. Variation of temperature as a function of time near and at the $\alpha \rightarrow \beta$ transformation point of titanium (Specimen 3). The points represent temperatures obtained from individual pyrometer readings. The time-axis origin is arbitrary.

obtained by averaging the individual points along the 'flat' portion of the plateau.

3. Results

The results of the present work are based on the International Practical Temperature Scale of 1968 [9]. In all computations, the geometrical quantities are based on their room temperature (295 K) dimensions.

Transformation Temperature: The individual temperatures along the initial flat portion (70–85%) of the plateau were averaged to obtain the transformation temperature for each specimen. The results, given in table 1, indicate that the average transformation temperature for the three specimens is 1166.4 K with an average absolute deviation from the mean of 0.8 K. At the transformation point of a given specimen, the standard deviation of an individual temperature from the mean is about 3 K which is about the same as the random fluctuations observed during the pyrometer calibration. It may be concluded that the temperature of the $\alpha \rightarrow \beta$ transformation in titanium is 1166 K.

TABLE 1. Experimental results for the $\alpha \rightarrow \beta$ transformation temperature and transformation energy of titanium

Specimen number	Heating rate ^a (K·s ⁻¹)	Transformation Temperature			Transformation energy (J·mol ⁻¹)
		Number of temp.	Temperature (K)	Standard dev. (K)	
1	2500	45	1167.7	2.5	—
2	2700	34	1166.2	3.0	4118
3	2600	44	1165.5	2.9	4222

^a Evaluated approximately 50 K below the transformation point.

Transformation Energy: The transformation energy was obtained from the time integral of the power absorbed by the specimen during the transformation. The time duration of the transformation was defined by intersections between the plateau and the linearly-fitted temperatures before and after the transformation. The absorbed power at a given instant of time was computed by subtracting the power loss due to thermal radiation from the power imparted to the specimen (voltage across the specimen times the current through the specimen). The thermal power radiated by the specimen was determined using an average value (0.27) for the hemispherical total emittance from the literature [10]. Even a considerable uncertainty (~10%) in the emittance value would not contribute significant errors to the absorbed power since the calculated radiative power loss from the specimens was always less than 1 percent of the imparted power at the transformation temperature.

The results for specimens 2 and 3 are given in table 1; in the case of specimen 1, the maximum temperature of the experiment was insufficient to establish the time variation of temperatures in the β -phase. The average of the results for the two specimens yields a value of 4170 J·mol⁻¹ for the $\alpha \rightarrow \beta$ transformation energy for titanium with an absolute deviation of 1.2 percent.

Electrical Resistivity: The variations of the electrical resistivity of a specimen with time and with temperature are shown in figures 3 and 4, respectively. The dashed lines in figure 4 represent linear fits to the data below and above the transformation point. The final resistivity values presented in table 2 were obtained by fitting (by the least squares method) the results for the specimens 2 and 3. It may be seen that the change in electrical resistivity during the transformation ($\alpha \rightarrow \beta$) is about 9 percent. Extrapolation of the resistivity values above the transformation point to 1500 K is in agreement, within 0.3 percent, with those reported in another publication [7].

Estimate of Errors: The methods of estimating errors in the measured and computed quantities have been discussed at length in an earlier publication [6]. Specific items in the error analysis were recomputed whenever the present conditions differed from those in the earlier publication. The estimated maximum errors in the reported values are: 7 K for the transformation temperature, 5 percent for the transformation energy, and 2 percent for the electrical resistivity.

TABLE 2. Experimental results for the electrical resistivity of titanium in the region of its $\alpha \rightarrow \beta$ phase transformation

α -phase		β -phase	
Temperature (K)	Resistivity ($\mu\Omega\cdot\text{cm}$)	Temperature (K)	Resistivity ($\mu\Omega\cdot\text{cm}$)
1100	159.5	1180	147.0
1120	160.3	1200	147.4
1140	161.0	1220	147.8
1160	161.8	1240	148.2
		1260	148.6
		1280	149.0
		1300	149.4

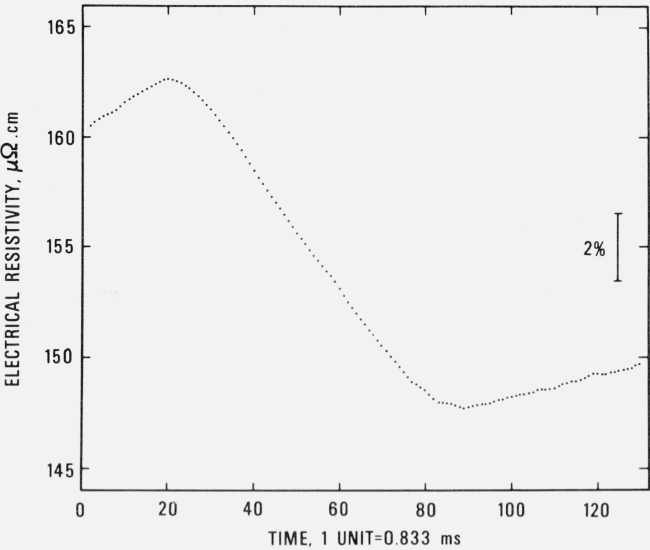


FIGURE 3. Variation of electrical resistivity as a function of time near and at the $\alpha \rightarrow \beta$ transformation point of titanium (Specimen 2). The points represent the resistivities obtained from individual data on current and voltage. The time-axis origin is arbitrary.

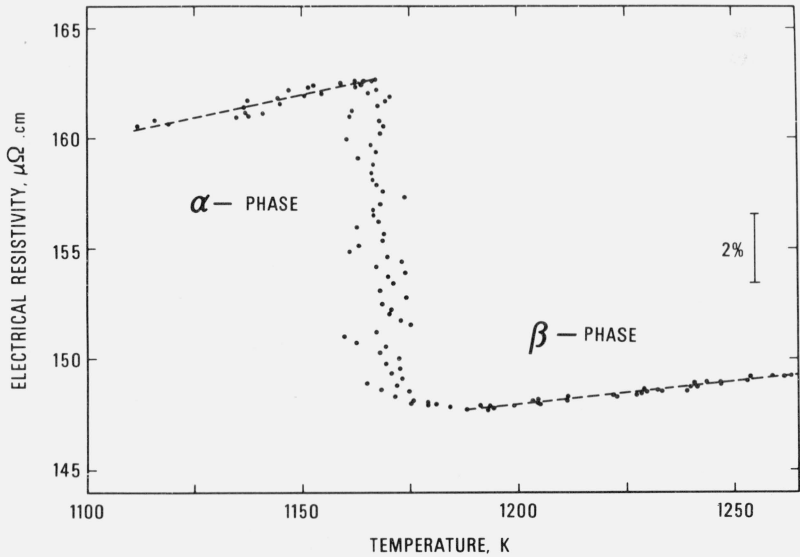


FIGURE 4. Variation of electrical resistivity as a function of temperature near and at the $\alpha \rightarrow \beta$ transformation point of titanium (Specimen 2). The points represent the resistivities obtained from individual data on current and voltage.

4. Discussion

The first evidence of a solid-solid transformation in titanium appeared in the electrical resistivity measurements by Schulze [11] in 1931. Later, DeBoer et al. [12] determined the nature of the transformation (hexagonal close-packed to body-centered cubic) by x-ray crystallography as well as the transformation temperature from a discontinuity in the electrical resistivity at 1155 ± 20 K. Since then, a number of other investigators have reported values for the temperature (and energy) associated with the $\alpha \rightarrow \beta$ transformation. The results are given in table 3 for comparison with the present work. The agreement between transformation temperature results reported prior to 1958 may not be as good as is suggested by the values given in the table since in a number of investigations the transformation was observed over a finite temperature range (several degrees to about 100 K), making the assignment of a unique temperature somewhat difficult and arbitrary; some investigators have selected the temperature at the beginning of the transformation ($\alpha \rightarrow \beta$ in heating or $\beta \rightarrow \alpha$ in cooling) while others have chosen the temperature at the end of the transformation.

The present value for the transformation temperature is higher than most of the values reported in the literature by about 10 K of which a few degrees can be attributed to possible differences in the temperature scales. The remaining discrepancy may partly be due to the high heating rates (of the order of 10^3 K·s⁻¹) used in this work. Pulse heating experiments on titanium by Parker [24] and by Martynyuk and Tsapkov [26] with even higher heating rates of the order of 10^5 and 10^7 K·s⁻¹, respectively, have indicated possible

superheating of the $\alpha \rightarrow \beta$ transformation by perhaps as much as 20 and 90 K, respectively.

The temperature-versus-time plateaus (~60 ms duration) obtained from our pulse heating experiments are believed to represent nearly complete $\alpha \rightarrow \beta$ transformation. This is substantiated by Parker's work in which he has shown that the phase change in titanium is very rapid, occurring in less than 200 μ s. The energy of transformation obtained in this work is 0.5 percent higher than the value of Kolhaas et al. [23], 2 percent higher than the value of Scott [20] and 12 percent higher than the value of Backhurst [21], all obtained by adiabatic calorimetry. Our result is 5 percent and 18 percent higher than transformation energy values determined by Kothen [17] and Golutvin [22], respectively, using enthalpy data obtained by drop calorimetry. Observations of the arrest in the heating rate and in the cooling rate during transformation by Schofield [19] and by Cormier and Claisse [25], respectively, yield respective energy values which are 18 percent and 23 percent lower than our result; their results, based on an estimated average heat capacity at the transformation point, do not appear to take into account the very large peak in the heat capacity [20, 21, 23] associated with the phase change. The transformation energy values of Parker [24] and of Martynyuk and Tsapkov [26] were derived from current and voltage oscillograms, yielding values which are 20 percent lower and 3 percent higher, respectively, than the present work.

The values 4170 J·mol⁻¹ for the transformation energy and 1166 K for the transformation temperature yield a value of 3.58 J·mol⁻¹·K⁻¹ for the entropy of the $\alpha \rightarrow \beta$ transformation in titanium. This compares favorably with the value

TABLE 3. Values for the temperature and energy of the $\alpha \rightarrow \beta$ transformation in titanium reported in the literature

Investigator	Ref. No.	Year	Specimen purity (%)	Transformation temperature ^a (K)	Transformation energy (J·mol ⁻¹)
De Boer et al.	12	1936	Iodide	1155 \pm 20	—
Greiner and Ellis	13	1949	99.9	1158	—
McQuillan	14	1950	99.93	1156	—
Duwez	15	1951	Iodide	1155 \pm 4	—
Worner	16	1951	99.93	1156 to 1160	—
Kothen	17	1952	99.96	1154	3946
Edwards et al.	18	1953	99.88	1157 \pm 4	—
Schofield	19	1956	Commercial	1158 and 1184	3400
Scott	20	1957	Iodide	1156 \pm 2	4090 \pm 100
Backhurst	21	1958	Commercial	—	3680
Golutvin	22	1959	Iodide	—	3430 \pm 80
Kolhaas et al.	23	1965	99.8	1167	4150
Parker	24	1965	99.9+	—	3350 \pm 200
Cormier and Claisse	25	1974	—	—	3200 \pm 400
Martynyuk and Tsapkov	26	1974	99.74	—	4300
Present work			99.9+	1166 \pm 7	4170 \pm 200

^a All temperatures and uncertainty limits in this table are those reported by the authors of the original papers. The majority of the reported temperatures were most likely based on IPTS-48, which would necessitate an addition of 1.6 K to correct them to IPTS-68.

3.47 J·mol⁻¹·K⁻¹ obtained earlier for the entropy of transformation for zirconium [2].

Figure 5 compares the values of electrical resistivity near and at the transformation point as reported in the literature; the changes in resistivity during the transformation as expressed by the ratio ρ_{\min}/ρ_{\max} are presented in table 4 along with the temperatures corresponding to maximum and minimum resistivities as well as the specimen purities used in the various investigations. Although there are considerable discrepancies between data reported by different investigators, all results, with the exception of those of Lampson et al. [31], show about the same relative change in resistivity (ρ_{\min}/ρ_{\max}) during the phase change. The resistivity values measured by Wyatt (specimen purity 99.74%) [27], Zhorov [28] and Arutyunov et al. [29] at temperatures outside of the transformation range are all approximately 2 percent higher than those obtained from the present work; the systematic differences may arise, at least in part, from the higher purity of our specimens. Other measurements by Wyatt (specimen purity 99.96%) however, and those of Unvala and Goel [3] and Lampson et al. [31] yield values which are about 17 percent above, 12 percent above and as much as 12 percent below the present results, respectively. Insofar as the discrepancies cannot be reconciled on the basis of specimen purity alone, it suggests that specimen contamination and/or measurement error may have been present in some of the investigations.

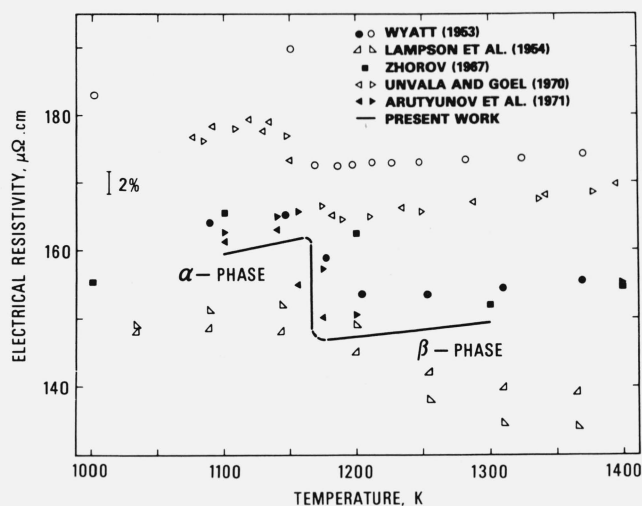


FIGURE 5. Values of electrical resistivity near and at the transformation point in titanium as reported in the literature.

The solid lines indicate the least-squares fits to our data. The symbols ∇ , \blacktriangleright , \triangle , and \blacktriangleleft , \triangleleft , refer to data taken during heating and cooling of the specimens, respectively. The symbols \circ and \bullet refer to measurements [27] on specimens with respective purities of 99.96 and 99.74 percent.

TABLE 4. Change of electrical resistivity of titanium during the $\alpha \rightarrow \beta$ transformation reported in the literature

Investigator	Reference	Year	Specimen purity (%)	Temp. of max. resistivity (K)	Temp. of min. resistivity (K)	Ratio, $\frac{\rho_{\min}}{\rho_{\max}}$
Wyatt	27	1953	99.96	1151	1186	0.91
Wyatt	27	1953	99.74	1146	1254	.93
Lampson et al.	31	1954	Commercial	1140	1350	.88
Zhorov	28	1967	99.8	1100	1300	.92
Unvala and Goel	30	1970	Commercial	1120	1182	.92
Arutyunov et al.	29	1971	99.8	1156	1200	.91
Martynuk and Tsapkov	26	1974	99.74	—	—	.92
Present work	.	.	99.9+	1163	1180	.91

5. References

- [1] Cezairliyan, A., and McClure, J. L., High Temp. Science **7**, 189-196 (1975).
- [2] Cezairliyan, A., and Righini, F., J. Res. Nat. Bur. Stand. (U.S.) **79A**, (Phys. and Chem.) No. 1, 81-84 (Jan.-Feb. 1975).
- [3] Cezairliyan, A., and McClure, J. L., High Temperatures-High Pressures **8**, 461-467 (1976).
- [4] Foley, G. M., Rev. Sci. Instr. **41**, 827-834 (1970).
- [5] Cezairliyan, A., J. Res. Nat. Bur. Stand. (U.S.) **75C**, (Eng. and Instr.), No. 1, 7-18 (Jan.-Mar. 1971).

- [6] Cezairliyan, A., Morse, M. S., Berman, H. A., and Beckett, C. W., J. Res. Nat. Bur. Stand. (U.S.) **74A**, (Phys. and Chem.) No. 1, 65-92 (Jan.-Feb. 1970).
- [7] Cezairliyan, A. and Miiller, A. P., Heat Capacity and Electrical Resistivity of Titanium in the Range 1500 to 1900 K by a Pulse Heating Method, High Temperatures-High Pressures, in press.
- [8] Cezairliyan, A., and Miller, A. P., J. Res. Nat. Bur. Stand. (U.S.), **82**, No. 2, 119-122 (Sept.-Oct. 1977).
- [9] International Practical Temperature Scale of 1968, Metrologia **5**, 35-44 (1969).

- [10] Thermophysical Properties of Matter, Vol. **7**, p. 723, ed. by Y. S. Touloukian and D. P. Dewitt (IFI/Plenum Press, New York-Washington, 1970).
- [11] Schulze, A., Ztsch. Für Metallkunde **23**, 261-264 (1931).
- [12] De Boer, J. H., Burgers, W. G., and Fast, J. D., Proc. Acad. Sci. Amsterdam **39**, 515-519 (1936).
- [13] Greiner, E. S. and Ellis, W. C., Trans. Amer. Inst. Min. Met. Eng. **180**, 657-665 (1949).
- [14] McQuillan, A. D., J. Inst. Metals **78**, 249-257 (1950).
- [15] Duwez, P., J. Metals **3**, 765-771 (1951).
- [16] Worner, H. W., Australian J. Sci. Res. **4**, 62-83 (1951).
- [17] Kothén, C. W., Ph.D. Thesis, Ohio State University, University Microfilms Publ. 52-23697, 1-89 (1952).
- [18] Edwards, J. W., Johnston, H. L., and Ditmars, W. E., J. Am. Chem. Soc. **75**, 2467-2470 (1953).
- [19] Schofield, T. H., J. Inst. Metals **85**, 68-70 (1956).
- [20] Scott, J. L., ORNL-2328, Oak Ridge Nat. Lab., July (1957).
- [21] Backhurst, L., J. Iron Steel Inst. (London) **189**, 124-134 (1958).
- [22] Golutvin, Yu. M., Russ. J. Phys. Chem. **33**, 164-168 (1959).
- [23] Kohlhaas, R., Braun, M. and Vollmer, O., Z. Naturforschg. **20a**, 1077-1079 (1965).
- [24] Parker, R., Trans. Met. Soc. (AIME) **223**, 1545-1549 (1965).
- [25] Cormier, M. and Claisse, F., J. Less-Common Metals **34**, 181-189 (1974).
- [26] Martynyuk, M. M. and Tsapkov, V. I., Russ. Metallurgy (Metally) **2**, 108-112 (1974).
- [27] Wyatt, J. L., J. Metals **5**, 903-905 (1953).
- [28] Zhorov, G. A., High Temp. (USSR) **5**, 881-888 (1967), see also ibid, High Temp. (USSR) **8**, 501-504 (1969).
- [29] Arutyunov, A. V., Banchila, S. N., and Filippov, L. P., High Temp. (USSR) **9**, 487-489 (1971).
- [30] Unvala, B. A., and Goel, T. C., Rev. Int. Hautes Tempér. et Réfract. **7**, 341-345 (1970).
- [31] Lampson, F. K., Rowe, G. H., Droher, J. J., and Draghie, J., U.S. AEC Publ. NEPA-1826, 1-10 (1954).